WebGasEOS 1.x User Guide

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1. Introduction

WebGasEOS, a free online application, provides a fast and robust means of computing real gas properties using common cubic equations of state. It utilizes the `RealGas_Properties` module, part of the TOUGH-Fx/TOUGH+ project (Moridis *et al.*, 2005). In addition to basic *PVTx* relationships, WebGasEOS offers derivative thermodynamic quantities, including fugacity coefficients, viscosities, binary diffusivities, and thermal conductivity. Using the interactive form, you may select an equation of state, specify temperature, pressure, and composition, choose properties of interest, and set convenient units. WebGasEOS will calculate real gas properties for one or a number of *T-P* points. Results can be generated interactively, or output in a columnar format for export to other applications.

Disclaimer

2. Using WebGasEOS

2.1 Inputs

The input to WebGasEOS is structured in the form of a worksheet, where inputs may be added/edited without stepping through menus or prompts. A properly configured browser should preserve all inputs and settings, with the standard browser BACK button returning to the original form (note: some versions of Internet Explorer are not consistent in this regard).

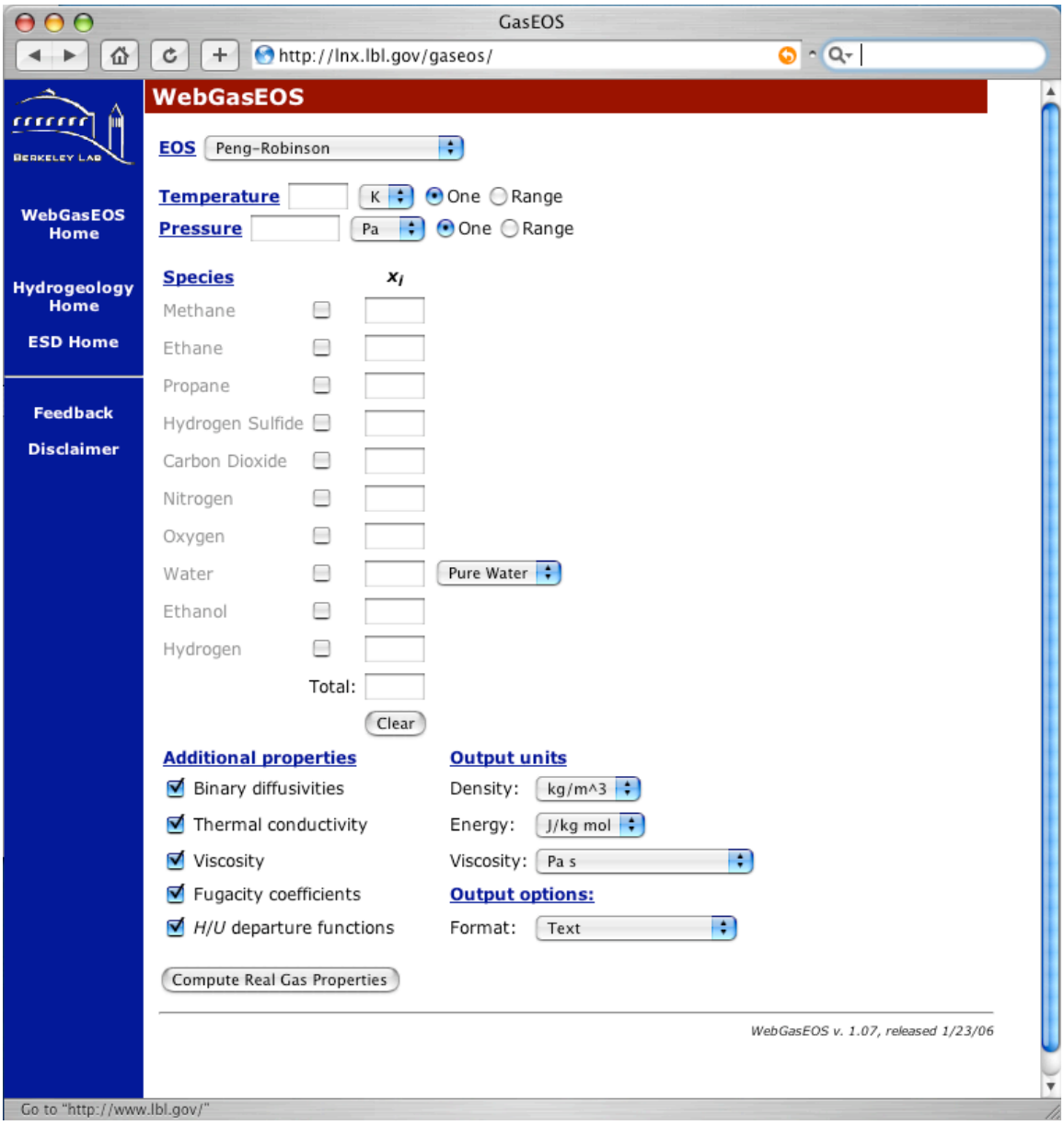

Figure 1: WebGasEOS worksheet.

The worksheet includes several input fields, seen in Figure 1:

EOS

The EOS field selects the equation of state used for the physical properties calculation. The choices include:

1. Redlich-Kwong EOS (RK): The Redlich-Kwong (1949) relation, a two-parameter pressure-explicit EOS based on the simple van der Waals expression.
2. Soave-Redlich-Kwong EOS (SRK): Soave (1972) modification of the RK relation, including a dependence on the Pitzer acentric factor in the attractive term.
3. Peng-Robinson EOS (PR): A more accurate EOS, with *T* and acentric-factor dependence in the attractive term and a more complex repulsive term. Can be applied to some liquid regions with usable accuracy (Peng and Robinson, 1976).
4. Peng-Robinson-Stryjek-Vera (PRSV): The Peng-Robinson EOS with modifications to the temperature and acentric factor dependence. Improves some polar-nonpolar mixture calculations and properties at low temperatures (Stryjek and Vera, 1986).

In WebGasEOS v1.x, a van der Waals (vdW) mixing rule is used to estimate multi-component EOS parameters.

Temperature and **Pressure**

These fields specify a temperature and pressure for the calculation (both are required). While, theoretically, all positive absolute temperatures and positive pressures are defined and accepted by the form, the practical *T* and *P* ranges are limited by the choice of EOS and the EOS parameters defined for each species. The units you select for input will also be used for the calculated physical properties produced in the output.

You may also select a range of temperatures or pressures (but not both) to perform multiple calculations, using the radio buttons to activate the option and specifying a maximum and increment. These values are preserved for future use, along with all other form inputs, even when the range feature is temporarily deactivated.

Species

The system of interest is defined by a set of species concentrations. To create a system:

1. Select the species of interest using the checkboxes
2. Specify the mole fraction of each species

WebGasEOS will add up the mole fractions and display the total. Mole fractions must add to approximately 1.000 (+/- 10^{-3}). The **clear** button will clear mole fraction

values for all species. The calculation will be performed only with the species you have selected via the checkboxes. You may select and deselect species without deleting the x_i field, preserving inputs for future calculations

Additional Properties

The checkboxes select additional properties to be calculated (default: compute all available properties). You may want to disable some or all of these features to give a simpler output, particularly for long temperature or pressure series.

Binary diffusivities: Binary diffusivities may only be calculated for binary systems. The low-pressure diffusivity is calculated via the method of Fuller, *et al.* (1969). High-pressure diffusivity is adjusted according to density and viscosity according to the method of Riazi and Whitson (1993).

Thermal conductivity: Calculates the thermal conductivity for the system as a whole. (Chung, 1984;1988)

Viscosity: Calculates the viscosity for the system as a whole, using the selected units (Chung, 1984;1988).

Fugacity coefficients: Calculates the fugacity coefficients (Φ) for each species.

***H*/*U* departure functions:** Computes the enthalpy and internal energy departure functions and total $\Delta H/\Delta U$ for each state of a series calculation with respect to State #1. For sets of two or more state points, GasEOS returns:

1. The ideal-gas (P=0 or V$\rightarrow\infty$) enthalpy and internal energy changes between T_1 and T_N.
2. The net enthalpy and internal energy departures to the ideal gas state at constant T from state #1 to state N, i.e.: $(H_1 - H_{ig}) - (H_N - H_{ig})$
3. The total enthalpy and internal energy changes from state #1 to state N, calculated using the departure functions: $\Delta H_{1\text{-}N} = (H_1 - H_{ig}) + \Delta H_{ig} - (H_N - H_{ig})$

Output units

Select the desired output units for density, energy (enthalpy and internal energy), and viscosity. The units selected for temperature and pressure inputs will be used in the output.

Output options

Select either a formatted text output, for onscreen viewing or printing, or a multicolumn data format. The multicolumn output is monospaced, with #-commented headers for use in many common graphing programs. The data may also be cut and pasted into any application.

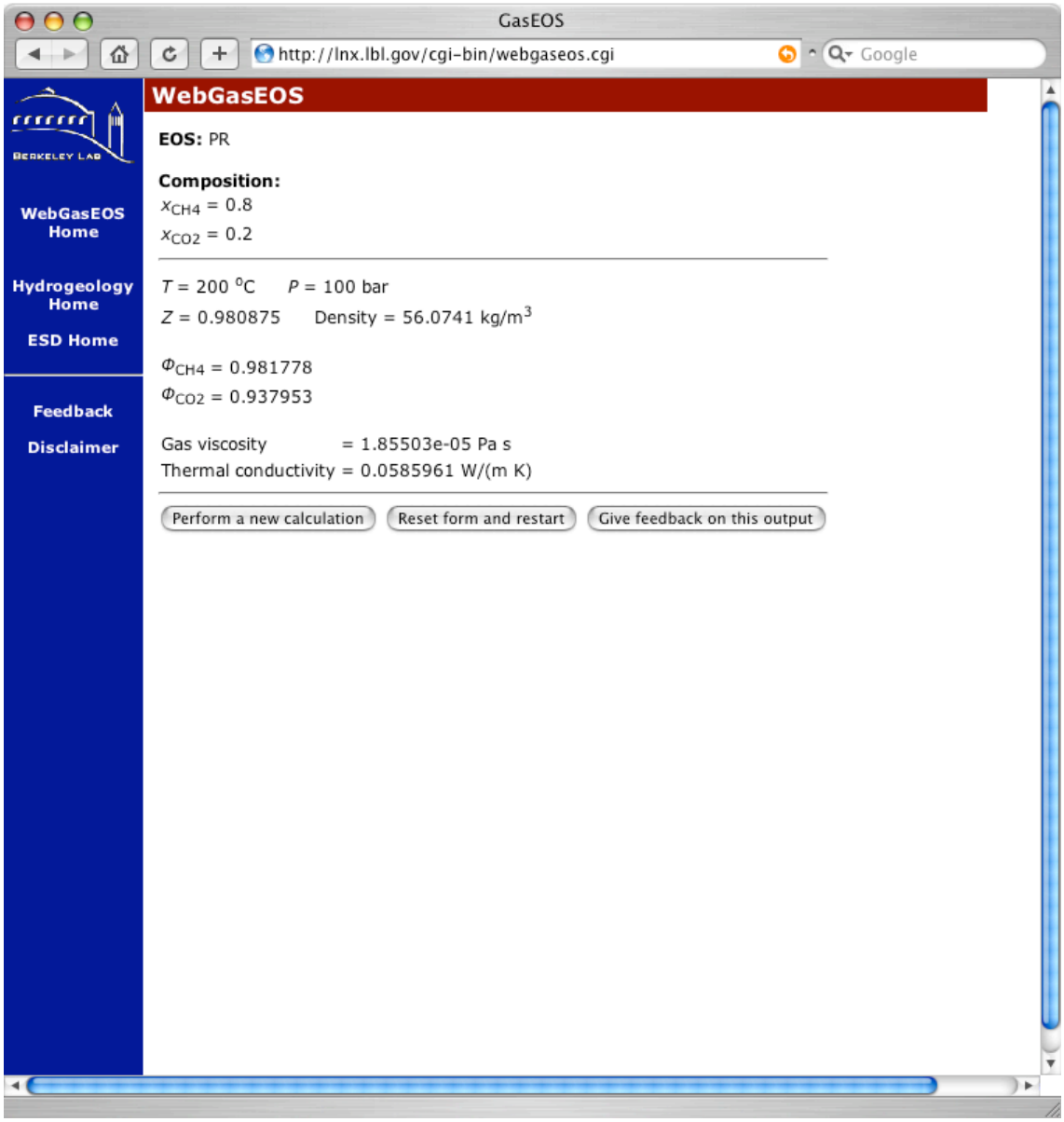

Figure 2: Sample WebGasEOS output, single point

2.2 WebGasEOS output

The **Compute Real Gas Properties** button submits the worksheet to the WebGasEOS application. For formatted text output (Figure 2), the application displays:

1. Selected EOS
2. Selected composition
3. Temperature and Pressure
4. Compressibility (single phase, or gas and liquid)

5. Density (single phase, or gas and liquid)

Plus any selected derivative properties, as specified in the input form. For multiple state points, the properties at each state are displayed, along with depature functions with respect to state #1, if selected (Figure 3).

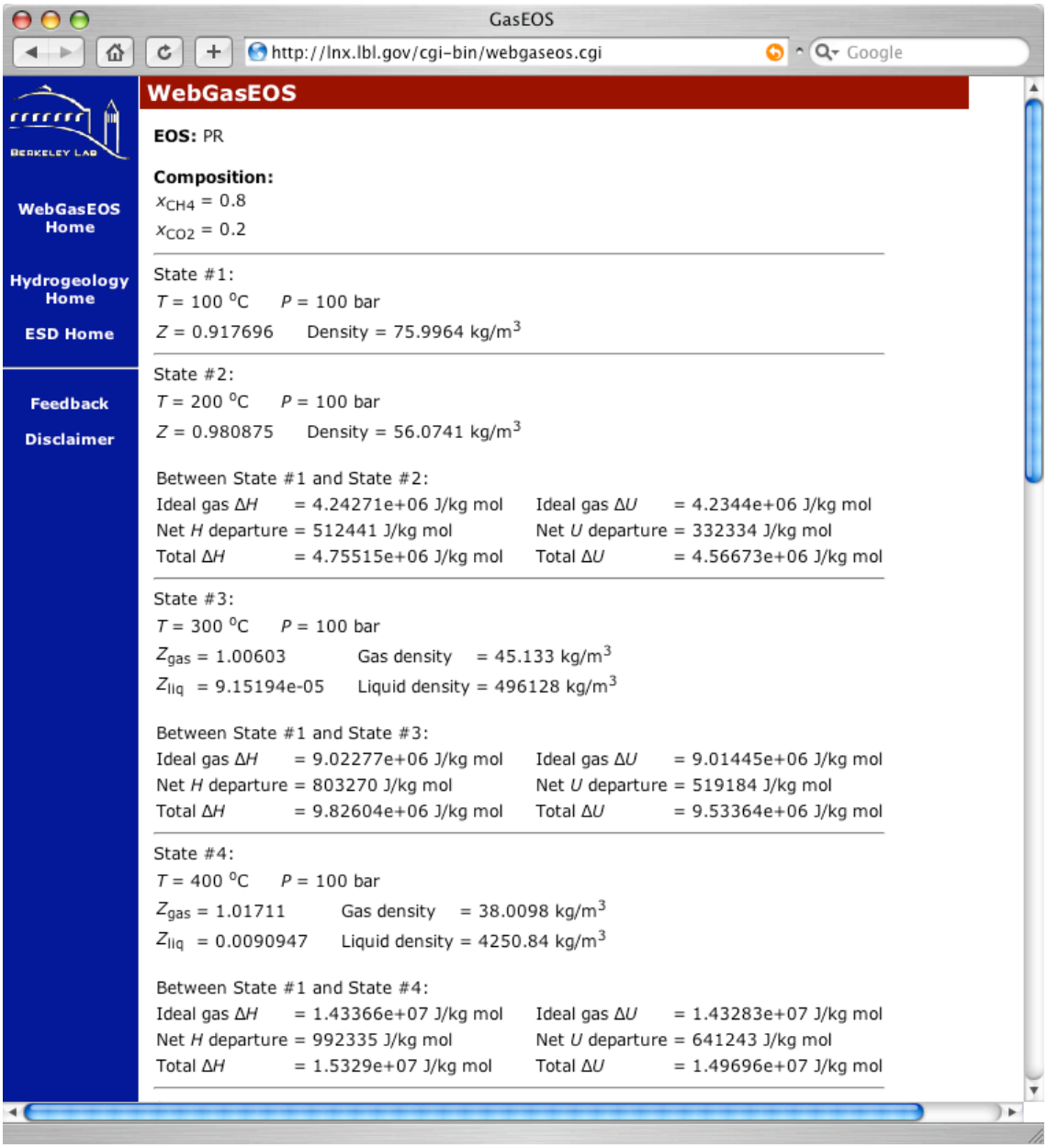

Figure 3: Sample WebGasEOS output for multiple state points, with departure functions.

Several checks are built into the WebGasEOS output parser:

"**Warning:** At X°C, *P*sat(H2O) = Y atm / x_{max}(H2O) ~ Z in the gaseous phase"

This warning is included in WebGasEOS to handle the unique and difficult

properties of water. GasEOS is intended to be a properties package for real and ideal gases, however, water is included due to its importance for hydrogeological and other processes. Great care must be used when estimating liquid water properties via generalized equations of state. Therefore, a correlation for the saturation pressure of water is checked at each temperature, and the mole fraction of water specified by the user is compared to

$x_{max} \sim P_{sat}(H2O) / P$

the approximate maximum mole fraction of water permitted in an gaseous phase. If $x(H2O) > x_{max}$, a warning is generated. This warning is independent of any phase-splitting indicated by the roots of the EOS. For accurate real-gas properties, reducing $x(H2O)$ below x_{max} is recommended, since cubic equations of state are not ideal for reproducing the properties of liquids or dense fluids.

"Note: $P_{sat}(H2O) > P$ / Liquid water not indicated"

To remain true to actual water properties while also maintaining consistency with EOS usage, we also check water saturation. If the temperature is too high for a liquid phase to exist at a given pressure, results referring to a liquid phase should be ignored.

3. Calculation Methods and Restrictions

The WebGasEOS application uses the `RealGas_Properties` module, part of the TOUGH-Fx/TOUGH+ project, and is documented in detail elsewhere [ref]. Users of the web-based application should be aware of the methods used and limitations of the equation-of-state calculation of properties.

3.1 Equations of state

The equations of state used in WebGasEOS are pressure-explicit cubic equations of state. After parameters are set for one or more species, temperature, and pressure, the roots of the EOS are determined. If three real roots are present, the largest volume root corresponds to the vapor phase and the smaller to the liquid phase, with the intermediate root having no physical meaning. If one root is generated, that is used to represent the vapor phase.

Extensive review literature (Valderrama, 2003) highlight the features and problems of many common equations of state. Of the equations offered in this application, the SRK and PR equations are the most commonly used and the most widely studied, and offer the most flexibility. These equations have been found suitable for nonpolar pure fluid densities at moderate to high pressures and low temperatures, and for enthalpic changes for gases at low pressures. The PR EOS has also shown promise for densities of polar species at moderate pressures and enthalpy calculations at moderate to high pressures. For mixtures, both the SRK and PR have similar applicability, using the default van der Waals mixing rules, for mixtures of polar and nonpolar components at low and high pressures, subject to the species parameter data available. We include the RK EOS for reference, although it is no longer used in serious physical properties applications. It may be used for calculations at low reduced pressure, including fugacities, and for calculating moderate departures from ideal behavior (Walas, 1985). We have also included a modified form of the PR equation, the PRSV (Stryjek and Vera, 1986) that includes an additional adjustable parameter to increase applicability at low temperatures. The PRSV will be coupled with extended mixing rules in future releases of the application to improve multicomponent, multiphase EOS calculations.

3.2 Fugacities

Gas fugacity coefficients are computed analytically from the EOS of choice though integration. For a pure component:

$$\ln\phi = Z - 1 - \ln Z - \frac{1}{RT}\int_{\infty}^{V}\left(P - \frac{RT}{V}\right)dV$$

For mixtures, we integrate the partial molar volume, $\overline{V}_i$, and have derived an analytical expression for partial fugacity coefficients from the pressure-explicit equations of state (Walas, 1985):

$$RT\ln\hat{\phi}_i = \int_V^{\infty}\left(\frac{\partial P}{\partial n_i} - \frac{RT}{V}\right)dV - RT\ln Z$$

In the case of mixtures, van der Waals mixing rules are the default method for determining EOS parameters.

3.3 Gas viscosities and thermal conductivities

Viscosities and thermal conductivities are computed via the correlations of Chung and collaborators (1984; 1988). The correlations are derived from kinetic gas theory, include the effects of molecular shape and intermolecular forces, and apply to a wide range of polar and nonpolar species. Density-dependent functions extend the applicability to dense gases and multicomponent mixtures, with average absolute deviations of 4% for viscosity predictions and 6% for thermal conductivity predictions. The parameters included in the `RealGas_Properties` module cover a wide range of temperatures and pressures, typically from subcritical to supercritical states over pressure ranges of 100 bar or greater (Chung, 1988).

3.4 Binary diffusivities

Low-pressure binary diffusivities are calculated via the method of Fuller (1969), using a correlation based on atomic diffusion volumes and fitted to actual experimental data (Fuller, 1966). The correlation is extended to higher pressures, dense fluids, and liquids using an additional correlation relating the ratio of high- and low-pressure diffusivities to the ratio of high- and low-pressure viscosities (Riazi and Whitson, 1993). The correlation has been tested to 400 bar and predicts diffusion coefficients to an absolute average deviation of 8% for gases and 15% for liquids. The low- and high-pressure viscosities and densities used in the correlation are calculated with the internal `RealGas_Properties` routines.

3.5 Enthalpy and internal energy departure functions

Total changes in enthalpy and internal energy are calculated explicitly. Between an initial state 1 and any other state point N the total energy change from 1-N is:

$$\Delta H_{1\text{-}N} = (H_1 - H_{ig}) + \Delta H_{ig} - (H_N - H_{ig})$$
$$\Delta U_{1\text{-}N} = (U_1 - U_{ig}) + \Delta U_{ig} - (U_N - U_{ig})$$

where:

$$\Delta H_{ig} = \int_{T_1}^{T_N} C_P(T)dT,\ \Delta U_{ig} = \int_{T_1}^{T_2} C_V(T)dT$$

derived analytically from the EOS. We use the pressure-explicit cubic equations of state with V and T as independent variables to construct departure functions from the real gas state to the ideal gas state. Assuming ideal gas behavior between an ideal gas state at V_{ig} and $V=\infty$, we integrate the EOS:

$$A_1(T,V) - A_{ig}(T,V_{ig}) = -\int_{\infty}^{V}\left(P - \frac{RT}{V}\right)dV + RT\ln\frac{V_{ig}}{V}$$

$$S_1(T,V) - S_{ig}(T,V_{ig}) = \left[\frac{\partial}{\partial T}\int_{\infty}^{V}\left(P - \frac{RT}{V}\right)dV\right]_V - R\ln\frac{V_{ig}}{V}$$

and

$$U - U_{ig} = (A - A_{ig}) + T(S - S_{ig})$$

$$H - H_{ig} = (U - U_{ig}) + PV - RT$$

for each departure, state 1 to ideal and state *N* to ideal (Tester, 1997).

4. Implementation

4.1 System requirements

The WebGasEOS application may be hosted on any web server with CGI gateway capability, local access to execute binaries as the server, and an F90/F95 compiler. It has been tested with Absoft Pro Fortran for OS X and Sun Fortran 95 using the open-source Apache HTTP server. The structure of the application is optimized for Linux, UNIX, and OS X (Darwin/OpenBSD) operating systems. The code is not validated for use with the GNU G95 Fortran compiler and has not been tested with other web server software or operating systems.

4.2 RealGasEOS package

The core of the physical properties calculation is the `RealGas_Properties` module, part of the TOUGH-Fx/TOUGH+ project (Moridis *et al.*, 2005). The module provides a set of customizable object-oriented routines that perform EOS calculations of *PVTx* properties and derived thermodynamic quantities.

4.3 WebGasEOS F90 application

The `RealGas_Properties` routines are called directly from a Fortran 90 handler routine. This code parses a formatted input file generated by the web application, initializes the EOS routines, computes one or a range of physical properties and thermodynamic quantities, and generates a formatted output file for use by the web application. The format of the input and output files are dependent on the feature set of the web application, and the two codes must be coordinated to match feature sets.

Since this code executes with webserver permissions, there is no communication with the user aside from the generation of the formatted output file. Error checking must be done through monitoring the appropriate system and server logs.

4.4 WebGasEOS CGI application

The web-based application executable is written in Perl, for widespread compatibility with popular web servers and CGI gateway configurations.

The program `webgaseos.cgi` parses form inputs submitted by the user's web browser, and so must be coordinated with the appropriate version of the WebGasEOS front-end web page. The Perl code accepts form inputs, performs required unit conversions, and creates a formatted input file for the WebGasEOS handler routine. The code uses standard POSIX routines to create and read unique temporary files in the server `/tmp` directory for communication with multiple instances of the program and manage user requests. After producing an input file, submitting a call to the WebGasEOS handler, and receiving the results, the application generates a customized web page to present the result. Modern, compliant HTML and CSS are used for cross-platform

compatibility, and the output has been tested on Safari for OS X, Mozilla/Firefox on Linux, Windows, and OS X, Lynx on Linux, and Internet Explorer for Windows and OS X. All EOS features are available on all platforms, although form input behavior may vary on browsers that do not comply with W3C and ECMA standards. A browser-resident cookie is checked created on starting the script, and new visitors to the application (those with no preset cookie) are logged in `/tmp/users.log`.

For initial installation, some internal fields must be customized to match the file system structure of the server (line numbers reflect WebGasEOS.cgi v1.06):

`my $SERVER = ""` (line 23): Set to the base URL of the server, without trailing slash

`system "/path/webgaseos $tmpfile $outfile";` (line 326): Set to the full absolute path of the WebGasEOS handler executable. It is recommended that the executable be placed in a secure location outside of the CGI-bin directory with only the privileges required for execution by the webserver.

`open OUT, ">>/tmp/users.log"` (line 706): Set to the full path of the WebGasEOS logfile (Default: `/tmp/users.log`).

4.5 WebGasEOS HTML/Javascript frontend

The user interacts with the WebGasEOS application through an HTML/CSS/Javascript frontend. The use and features are described in Section 2. Features relevant to installation or customization include:

- The code uses Javascript for client-side form validation. The validity of the user's selections are checked as they are entered, or before the form is submitted, and necessary alerts are issued. The form is functional without Javascript, or in the case of nonstandard script parsing—however, full client-side verification in Javascript prevents errors at the server level that might confuse users or create incorrect output.

- The code uses standard Javascript functions to set and read browser cookies on the client side. These contain no user information, but rather act as a flag. Visitors who execute the CGI application without a preexisting cookie will have their IP address logged in the `users.log` file.

- The layout is primarily through CSS styles. There is no global external style sheet in version 1.x, so relevant styles are duplicated into the CGI application to match look and feel between input and output.

- The input worksheet is defined using HTML FORM tags and organized via HTML TABLEs. The CGI application does not need to know the structure of the input worksheet, only which variables to extract. Species data are structured as arrays, both in the Javascript validation functions and in the data the form sends to the CGI

gateway. Adding additional species requires consistent revisions to all three WebGasEOS components, but no structural changes.

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